Low-energy spin dynamics in the $[YPc_2]^0$ $S = 1/2$ antiferromagnetic chain

F. Branzoli[1], P. Carretta[1], M. Filibian[1], S. Klyatskaya[2] and M. Ruben[2]
[1]*Department of Physics "A. Volta", University of Pavia-CNISM, 27100 Pavia (Italy) and*
[2]*Institute of Nanotechnology, Karlsrhue Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen (Germany)*

^{1}H nuclear magnetic resonance (NMR) measurements in $[YPc_2]^0$, an organic compound formed by radicals stacking along chains, are presented. The temperature dependence of the macroscopic susceptibility, of the NMR shift and of the spin-lattice relaxation rate $1/T_1$ indicate that the unpaired electron spins are not delocalized but rather form a $S = 1/2$ antiferromagnetic chain. The exchange couplings estimated from those measurements are all in quantitative agreement. The low-energy spin dynamics can be described in terms of diffusive processes and the temperature dependence of the corresponding diffusion constant suggests that a spin-gap around 1 K might be present in this compound.

PACS numbers: 76.60.Es, 75.10.Pq, 75.40.Gb, 75.10.Jm

I. INTRODUCTION

Molecular solids have attracted much interest since decades owing to the possibility to easily tune their properties either through a chemical bottom up approach or by varying physical parameters as the external pressure.[1] One of the most versatile families of molecular solids is the one based on phthalocyanine (Pc= $C_{32}H_{16}N_8$) molecules.[2] In fact, the employment of these materials in different areas, ranging from the fabrication of organic light emitting diodes, to contrast agents or spintronics materials, has been envisaged. Pc-based compounds have attracted significant interest in the last decade after it has been suggested that high temperature superconductivity could be induced in these materials by alkali doping[3] and, more recently, when it has been recognized that neutral $[LnPc_2]^0$ molecules, with Ln a lanthanide ion, are molecular nanomagnets with extremely long coherence times at liquid nitrogen temperature.[4–8] Owing to the flat shape of Pc molecules, the structure of Pc-based materials is typically characterized by chains along which Pc molecules tend to stack.[9] Accordingly some of the Pc-based materials show many similarities to the Beechgaard salts.[10]

Bis(phthalocyaninato) yttrium $[YPc_2]^0$ compound can be considered the parent compound of the aforementioned $[LnPc_2]^0$ molecular magnets. In fact, it is characterized by the absence of localized f electrons and the microscopic properties are mainly associated with the presence of an unpaired electron delocalized in the a_2 π orbital, due to the one-electron oxidation of the $[YPc_2]^-$ unit.[11] Thus, $[YPc_2]^0$ allows to investigate the spin dynamics associated only with this unpaired electron spin, independently from the one due to f electrons. One of the most suitable tools to address this aspect is nuclear magnetic resonance (NMR) technique. In this work we present an experimental study of the magnetic properties of $[YPc_2]^0$ compound by means of magnetization and nuclear magnetic resonance (NMR) measurements. The temperature dependence of the macroscopic susceptibility, of the NMR shift and of the spin-lattice relaxation rate $1/T_1$ clearly show that this system is a prototype of a $S = 1/2$ antiferromagnetic chain, characterized by a diffusive low-frequency spin dynamics and, possibly, by the presence of a low-energy spin-gap.

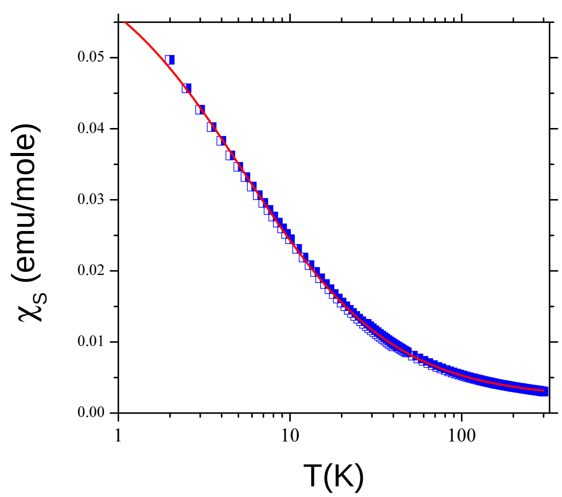

FIG. 1: Temperature dependence of static uniform susceptibility χ_S for $[YPc_2]^0$ complex, derived from SQUID magnetization measurements. The solid line shows the best fit of the data to Curie-Weiss law.

II. EXPERIMENTAL RESULTS AND DISCUSSION

$[YPc_2]^0$ polycristalline samples were synthesized by using some modifications of the protocol published in Ref. 12. All reagents were purchased from Across or Aldrich and used without further purification. A mixture of 1,2-dicyanobenzene (42 mmol), $Y(acac)_3 \cdot 4H_2O$ (5 mmol), and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) (21 mmol) in 50 mL of 1-pentanol was refluxed for 1.5 days. The solution was allowed to cool to room temperature. The precipitate was collected by filtration and washed with n-hexane and Et_2O. The crude purple product was redissolved in 800 ml of $CHCl_3/MeOH$ (1/1) and undissolved PcH_2 was filtered off. Both forms, blue (anionic

$[YPc_2]^-$) and green (neutral $[YPc_2]^0$), were obtained simultaneously, as revealed by electronic absorption spectra. In order to convert the unstabilized anionic form to the neutral one, the reaction mixture was presorbed on active (H_2O-0%) basic alumina oxide. Purification was carried out by column chromatography on basic alumina oxide (deactivated with 4.6% H_2O, level IV) with chloroform methanol mixture (10:1) as eluent. In general, the yield was 30-35%. According to microelemental analysis based on atomic spectroscopic methods (ICP) performed at *Mikroanalytisches Labor Pascher*, the powder sample contains molecules of $[YPc_2]^0$, water and CH_2Cl_2 in ratio 1:1:1/3. The molecules crystallized in the space group $P2_12_12_1$ (γ-phase), as reported in Ref. 13.

DC magnetization (M) measurements have been performed by using an MPMS-XL7 Quantum Design superconducting quantum interference device (SQUID) magnetometer. The magnetization was found to depend linearly on the magnetic field intensity H, for $H \leq 5$ kGauss, over all the explored temperature range and, accordingly, the macroscopic static uniform susceptibility can be written as $\chi_S = M/H$. The temperature dependence of χ_S reveals the presence of antiferromagnetic correlations. In fact, χ_S(T) can be nicely reproduced by a Curie-Weiss (CW) law

$$\chi_S(T) = \frac{C}{T+\Theta} + \chi_0 \quad , \tag{1}$$

where $C = g^2\mu_B^2 S(S+1)N_A/(3k_B)$ is Curie constant (μ_B the Bohr magneton, g the Landé factor, N_A Avogadro's number and k_B Boltzmann constant). Θ is the CW temperature and χ_0 a temperature independent term mainly due to diamagnetic and Van-Vleck corrections. By fitting the data, leaving all three parameters free, we found an antiferromagnetic CW temperature $\Theta = 5.37 \pm 0.04$ K (Fig. 1) and a Curie constant $C = 0.342 \pm 0.002$ erg $\cdot$ K/G^2, quite close to the value 0.375 erg$\cdot$K/G^2, expected for a $S = 1/2$ system. If we fixed $C = 0.375$ erg$\cdot$K/G^2 the fit was still good and the CW temperature $\Theta = 6.18 \pm 0.03$ K. The temperature dependence of χ_S shows that the unpaired electron spins are localized along the chains formed by $[YPc_2]^0$ molecules, although a certain overlap of the π orbitals of adjacent molecules must be present in order to justify the magnitude of the antiferromagnetic exchange coupling J_e. In fact, although this system should present a narrow half-filled band, the sizeable Hubbard Coulomb repulsion $U \sim 1eV$ prevents the electron delocalization along the chain.[14] In this limit, $J_e = \Theta = 4t^2/U$, with t the hopping integral among adjacent molecules. From the estimated value of Θ one would derive a band width formed by the overlap of a_2 orbitals in adjacent molecules $W = 4t \sim 0.05$ eV$\ll U$, justifying the spin localization along the chain.

The ^{1}H NMR spectra were obtained in the 1.6-300 K temperature range for magnetic field intensities $H = 9$ T, 1 T and 0.3 T. The spectra were derived from the Fourier transform of half of the echo formed after a $\pi/2 - \tau - \pi$ pulse sequence, when the full NMR line could be irradiated or, otherwise, from the envelope of the echo amplitude upon varying the irradiation frequency. The lineshape was gaussian in all the investigated temperature range. For $H = 9$ T and $H = 1$ T a broadening of the spectrum can be observed at low temperature, which is more pronounced at higher field intensities (Fig. 2). On the other hand, for $H = 0.3$ T the linewidth $\Delta\nu$ is practically temperature independent and the broadening is likely to be due just to nuclear dipole-dipole interaction. The increase of the linewidth with H suggests that the low temperature line broadening originates from some anisotropy in the hyperfine coupling, which for a powder gives rise to a linewidth proportional to the susceptibility. In fact, it is noticed that if we subtract the T-independent contribution at $H = 0.3$ Tesla from the raw data and divide the linewidth by the Larmor frequency ν_0, the data at different fields overlap (inset to Fig.2). This result also indicates that there is not an additional internal field due to the onset of a long-range magnetic order down to 1.6 K.

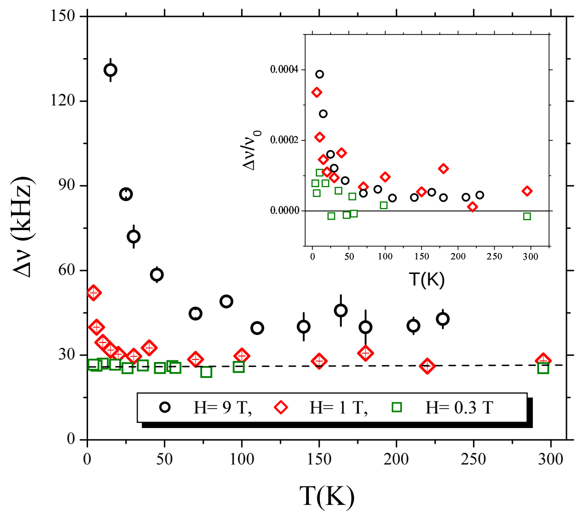

FIG. 2: Temperature dependence of ^{1}H full NMR linewidth at half intensity in $[YPc_2]^0$, at three different magnetic fields. In the inset the linewidth is normalized by the Larmor frequency after subtracting the constant linewidth due to nuclear dipole-dipole interaction.

The NMR paramagnetic shift $\Delta K = (\nu_R - \nu_0)/\nu_0$, with ν_R the resonance frequency, shows a more pronounced temperature dependence (Fig. 3). As expected, it was found to increase upon cooling, according to

$$\Delta K = \frac{A\chi_S}{2\mu_B N_A} \quad , \tag{2}$$

namely the temperature dependence of ΔK should be the same of the macroscopic spin susceptibility. In fact, also $\Delta K(T)$ is found to obey a Curie-Weiss law with a Curie-Weiss temperature $\Theta = 7.4K \pm 0.3$ K, close to the one derived from SQUID magnetization measurements. The small difference between those two type of measure-

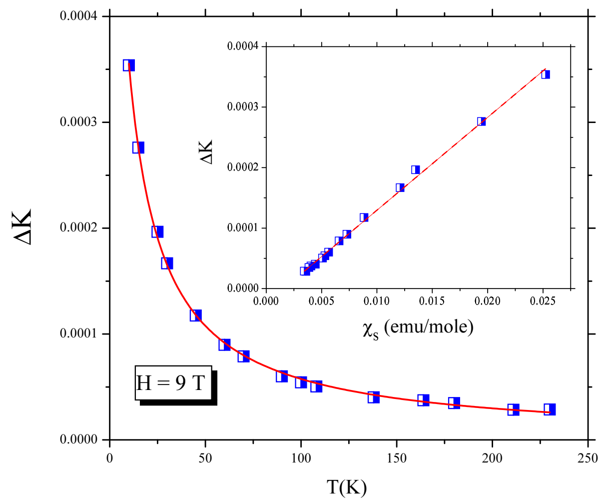

FIG. 3: Temperature dependence of ^{1}H paramagnetic shift ΔK in $[YPc_2]^0$. The solid line shows the best fit of the data to Curie-Weiss law. In the inset ΔK is reported as a function of the macroscopic susceptibility. The solid line is the best fit according for a linear dependence of ΔK vs χ_S.

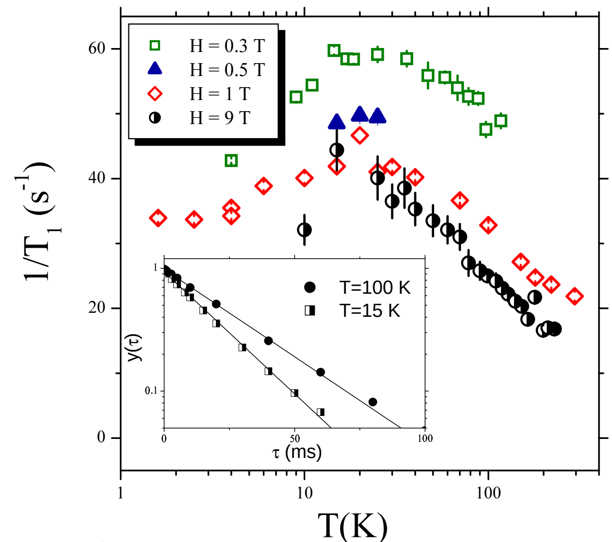

FIG. 4: ^{1}H nuclear spin-lattice relaxation rate temperature dependence for $[YPc_2]^0$ compound measured for different values of the applied field. In the inset the recovery of the nuclear magnetization as a function of the delay τ between the saturating and the echo readout sequences is shown at two different temperatures. The solid lines show the best fit for a single exponential recovery.

ments could be associated with a tiny amount of impurities which might affect the macroscopic susceptibility. Accordingly, the measurement of the microscopic susceptibility with paramagnetic shift measurements is expected to provide a more reliable estimate of the static uniform spin susceptibility and of the Curie-Weiss temperature. By plotting ΔK as a function of χ_S a linear trend is attained (Fig. 3) and from the slope it is possible to estimate the isotropic term of the hyperfine coupling tensor $A = 180 \pm 10$ Gauss.

The ^{1}H nuclear spin-lattice relaxation rate $1/T_1$ was measured in the 1.6 - 300 K temperature range and for different values of the external field. $1/T_1$ was extracted from the recovery of nuclear magnetization after a saturation recovery pulse sequence. The recovery law was found to be a single exponential in all the explored temperature range (Fig. 4, inset). This result is an evidence that the unpaired electron is delocalized onto a π orbital within the molecule. In fact, since in the two phthalocyanine rings a large number of inequivalent proton sites is present, if the electron was on a more localized orbital a distribution of hyperfine couplings would be present and, accordingly, a stretched exponential recovery law should be observed. Moreover, the fact that hyperfine coupling seems quite isotropic indicates that it could originate from the contact interaction between the unpaired electron spin in the a_2 π orbital and the ^{1}H nuclei.

The temperature dependence of $1/T_1$ at different magnetic fields is shown in Fig. (4). In general, for a relaxation process driven by electron spin fluctuations one can write

$$\frac{1}{T_1} = \frac{\gamma^2}{2N} \sum_{\alpha,\mathbf{q}} (|A_{\mathbf{q}}|^2 S_{\alpha,\alpha}(\mathbf{q},\omega_L))_{\perp} \quad , \qquad (3)$$

where γ is the nuclear gyromagnetic ratio, $|A_{\mathbf{q}}|^2$ the form factor describing the hyperfine coupling with spin excitations at wave-vector $\mathbf{q}$ and $S_{\alpha,\alpha}(\mathbf{q},\omega_L)$ ($\alpha = x, y, z$) the component of the dynamical structure factor at the Larmor frequency. In the high temperature limit, namely when the thermal energy is much larger than the exchange energy ($T \gg \Theta$), the $1/T_1$ of a spin $S = 1/2$ antiferromagnet becomes temperature and field independent and is given by[15]

$$\frac{1}{T_1} = \frac{\gamma^2}{2}(A_x^2 + A_y^2)\frac{S(S+1)}{3}\frac{\sqrt{2}\pi}{\omega_H} \quad , \qquad (4)$$

where $A_x \simeq A_y \simeq A$ are the components of the hyperfine coupling tensor which is basically isotropic, while $\omega_H = (J_e k_B/\hbar)\sqrt{2zS(S+1)/3}$ is the Heisenberg exchange frequency, with $z = 2$ the number of nearest neighbour spins along the chain. By taking the measured value of $1/T_1 \simeq 20$ s^{-1} at high temperature, from Eq. (4) it is possible to estimate the exchange frequency $\omega_H \simeq 9.2 \cdot 10^{11}$ rad/s, corresponding to an exchange coupling constant $J_e \simeq 7.0$ K, in quite good agreement with the value which can be estimated from the NMR shift measurements. Upon decreasing the temperature, for 200 K$\geq T \geq 30$ K, one observes a progressive slow increase of $1/T_1$ (Fig. (4)). In particular, it is noticed that nuclear spin-lattice relaxation rate increases on decreasing temperature according to

$$1/T_1 \propto ln^{1/2}(T_0/T) \quad . \qquad (5)$$

In fact, in Fig. (5) one observes that $(1/T_1)^2$ is a linear function of $1/T$, when reported in logarithmic scale. Remarkably, this logarithmic increase of $1/T_1$ is expected in

a $S = 1/2$ Heisenberg antiferromagnet, but for $T \leq J_e$[16]. Here it is not clear why the logarithmic behavior extends up to $T \gg J_e$.

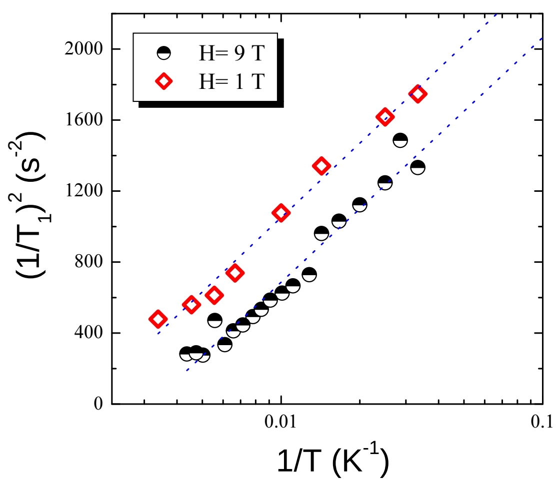

FIG. 5: The $1/T_1$ squared is plotted as a function of T^{-1}, in logarithmic scale, for two values of the external field (H = 9 T, circles and H = 1 T, squares). The dashed lines represent the best fits to Eq. (5).

At about 20 K a peak in the nuclear spin-lattice relaxation rate appears (Fig. 4), whose intensity decreases by increasing the external field intensity. Eventually, below $T \simeq 5$ K, the $1/T_1$ is only weakly temperature dependent. The maximum in $1/T_1$, not associated with molecular motions, could be due to a form factor, which partially filters out the antiferromagnetic fluctuations as the system gets more and more correlated.

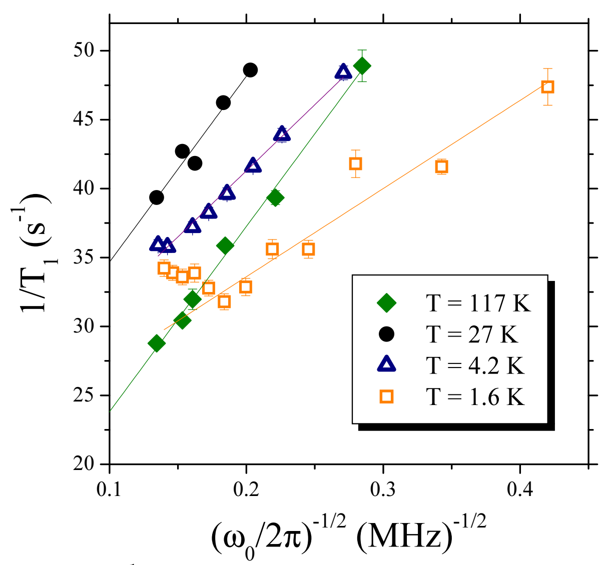

FIG. 6: The ^{1}H spin-lattice relaxation time $1/T_1$ in $[YPc_2]^0$ is plotted as a function of $(\omega_0/2\pi)^{-1/2}$ for different selected temperatures. The solid lines show the best fit according to Eqs.6 and 7 in the text.

The magnetic field dependence of $1/T_1$ (Fig. 6) can originate from the diffusive nature of the spin correlation function, which in one dimension is characterized by long-time tails yielding to a divergence of the low-frequency spectral density $J(\omega)$.[17] In fact, in the presence of diffusive processes for the spin excitations $1/T_1$ can be written in terms of the spectral density for the spin excitations according to the following equation[18]:

$$\frac{1}{T_1} = \frac{\gamma^2}{2} \frac{k_B T \chi_0}{(g\mu_B)^2} \left[\frac{3}{5} A_d^2 J(\omega_0) + \left(A^2 + \frac{7}{5} A_d^2 \right) J(\omega_e \pm \omega_0) \right] \quad , \tag{6}$$

where A_d is the anisotropic term of the hyperfine coupling, which hereafter shall be neglected since $A^2 \gg A_d^2$. Then just the second term in square bracket can be considered. In Eq.6 χ_0 is the static uniform susceptibility per spin and $\omega_e = \omega_0 \gamma_e / \gamma$ is the electron resonance frequency. This means that during the nuclear relaxation process a simultaneous flip of the electron and nuclear spins occur, involving an energy exchange $\hbar(\omega_e \pm \omega_0)$, and $1/T_1$ thus probes the spin excitations at a frequency close to ω_e.

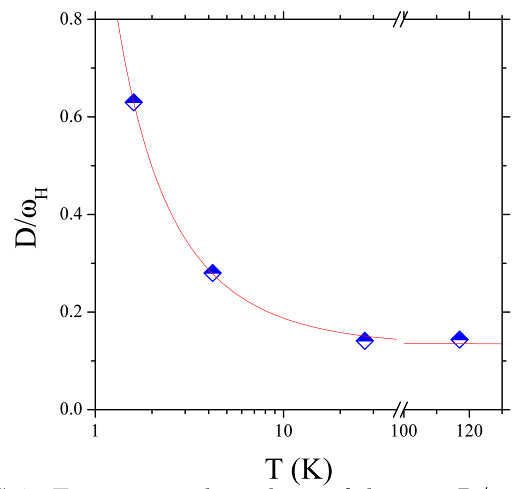

FIG. 7: Temperature dependence of the ratio D/ω_H between the spin diffusion coefficient D and the exchange frequency ω_H in $[YPc_2]^0$ compound as derived from the slopes in the $1/T_1$ vs $(\omega_0/2\pi)^{-1/2}$ plots in Fig. 6. The solid line gives the best fit according to $D \propto exp(\Delta/T)$ with $\Delta = 1.2 \pm 0.4$ K.

In a one dimensional system, the spectral density at ω_e is characterized by a low-frequency divergence given by[19]

$$J(\omega_e) = \frac{1}{\sqrt{2D}} \left(\frac{\omega_c + \sqrt{\omega_e^2 + \omega_c^2}}{\omega_e^2 + \omega_c^2} \right)^{1/2} \quad , \tag{7}$$

where ω_c is a low-frequency cutoff accounting for the finite spin anisotropy and/or inter-chain coupling, while D is the spin diffusion rate. In Fig. (6), the $1/T_1$ is plotted as a function of $\nu_0^{-1/2}$. The observed linear trend further proves the one-dimensional nature of the antiferromagnetic correlations. Moreover, the absence of a low-frequency flattening in $1/T_1$ plot indicates that

spin diffusion occurs in the electronic frequency range $\omega_c \ll \omega_e \ll D$. Thus, from the slopes of the curves it is possible to deduce the spin diffusion coefficient at different temperatures (Fig. 7) considering $A \simeq 180$ Gauss and neglecting $\omega_c \ll \omega_e$ in Eqs (6-7). The estimated spin diffusion coefficient is of the order of the exchange frequency ω_H and it is found to progressively decrease with temperature and to become nearly constant above 20 K. It is interesting to observe that $D \propto exp(\Delta/T)$, namely the behaviour expected for one-dimensional antiferromagnets in the presence of a spin-gap Δ between singlet and triplet excitations.[20] Here we find that $\Delta = 1.2 \pm 0.4$ K suggesting that a small gap, either due to competing exchange interactions or to a dimerization might be present in $[YPc_2]^0$. It is interesting to observe that, at low temperature, when the Zeeman energy $\hbar\omega_e \simeq \Delta$ the breakdown of Eq.7 is noticed. In fact, in Fig. (6) one clearly notices that at $T = 1.6$ K the linear behaviour is no longer obeyed at high fields (i.e. low values for $\sqrt{2\pi/\omega_0}$) and $1/T_1$ ceases to decrease with increasing field. This could be due to the modifications in the spin correlations induced by the magnetic field for $\hbar\omega_e \simeq \Delta$, possibly associated with the progressive closure of the spin gap.

In conclusion, from magnetization, ^{1}H NMR paramagnetic shift and T_1 measurements we have derived the magnitude of the antiferromagnetic exchange interaction in $[YPc_2]^0$ compound and found an overall good agreement. The low-energy spin excitations are of diffusive character and characteristic of one-dimensional antiferromagnets. From the temperature dependence of the spin diffusion rate derived from $1/T_1$ vs. H measurements it was found that a spin-gap around 1 K might be present in this compound.

Acknowledgements

The research activity in Pavia was supported by Fondazione Cariplo (Grant N. 2008-2229) research funds.

[1] see M. Scwoerer and H.C. Wolf in *Organic Molecular Solids*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2007)
[2] see *The Porphyrin Handbook* Vol. 19, K.M. Kadish, K.M. Smith, R. Guilard, Academic Press New York (2000)
[3] E. Tosatti, M. Fabrizio, J. Tóbik, and G.E. Santoro, Phys. Rev. Lett. **93**, 117002 (2004).
[4] F. Branzoli, M. Filibian, P. Carretta, M. Ruben and S. Klyatskaya, Phys. Rev. B **79**, 220404 (2009)
[5] F. Branzoli, P. Carretta, M. Filibian, G. Zoppellaro, M. J. Graf, J. R. Galan-Mascarós, O. Fuhr, S. Brink and M. Ruben, J. Am. Chem. Soc. **131**, 4387 (2009)
[6] S. Takamatsu, T. Ishikawa, S. Koshihara and N. Ishikawa, Inorg. Chem. **46**, 7250 (2007)
[7] N. Ishikawa, Y. Mizuno, S. Takamatsu, T. Ishikawa and S. Koshihara, Inorg. Chem. **47**, 10217 (2008)
[8] F. Branzoli, P. Carretta, M. Filibian, M. J. Graf, S. Klyatskaya, M. Ruben, F. Coneri, and P. Dhakal, Phys. Rev. B **82**, 134401 (2010)
[9] Y. Taguchi, T. Miyake, S. Margadonna, K. Kato, K. Prassides, and Y. Iwasa, J. Am. Chem. Soc. **128**, 3313 (2006).
[10] K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen and N. Thorup, Solid State Commun. **33**, 1119 (1980)
[11] R. Rousseau, R. Aroca and M.L. Rodriguez-Mendez, J. Mol. Struct. **356**, 49 (1995)
[12] M. Moussavi, A. De Cian, J. Fischer and R. Weiss, *Inorg. Chem.* **27**, 1287 (1988); N. Koike, H. Uekusa, Y. Ohashi, C. Harnoode, F. Kitamura, T. Ohsaka and K. Tokuda, *Inorg. Chem.* **35**, 5798 (1996); K. Kasuga, M. Tsutsui, R. C. Petterson, K. Tatsumi, N. Van Opdenbosch, G. Pepe and E. F. J. Meyer, J. Am. Chem. Soc. **102**, 4835 (1980).
[13] K. Katoh, Y. Yoshida, M. Yamashita, H. Miyasaka, B.K. Breedlove, T. Kajiwara, S. Takaishi, N. Ishikawa, H. Isshiki, Y.F. Zhang, T. Komeda, M. Yamagishi and J. Takeya, J. Am. Chem. Soc. **131**, 9967 (2009)
[14] M. S. Liao and S. Scheiner, J. Chem. Phys. **114**, 9780 (2001).
[15] T. Moriya, *Prog. Theor. Phys.* **16**, 23 (1956).
[16] M. Takigawa, O. A. Starykh, A. W. Sandvik and R. R. P. Singh, Phys. Rev. B **56**, 13681 (1997).
[17] H. Benner and J. P. Boucher, in *Magnetic Properties of Layered Transition Metal Compounds*, edited by L. J. De Jongh (Kluwer Academic, Norwell, MA, 1990), p. 323
[18] F. Devreux, J. P. Boucher and M. Nechtschein J. Phys. France **35**, 271 (1974).
[19] G. Soda, D. Jerome, M. Weger, J. Alizon, J. Gallice, H. Robert, J.M. Fabre and L. Giral, J. Phys. France **38**, 931 (1977); L. J. Azevedo, J. E. Schirber and J. C. Scott, Phys. Rev. Lett. **49**, 826 (1982).
[20] K. Damle and S. Sachdev, Phys. Rev. B **57**, 8307 (1998)